

PATENT SPECIFICATION

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(54) ISONONANOLS AND THEIR USE IN THE FORM OF BIS-ISONONYL ESTERS OF PHTHALIC ACID OR ADIPIC ACID AS PLASTICIZERS FOR POLYVINYL CHLORIDE

- (71) We, BADISCHE ANILIN- & SODA - FABRIK AKTIENGESELLSCHAFT, a German joint stock company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—
- 10 This invention relates to isononanols and their use in the form of bis-isononyl esters of phthalic acid or adipic acid as plasticizers for polyvinyl chloride.
- 15 Phthalic or adipic esters of C_4 to C_{10} alkanols are used to a great extent as plasticizers for polyvinyl chloride. Phthalic and adipic esters of C_4 to C_{10} alcohols, particularly 2-ethylhexanol, nonanols and decanols, have acquired particular importance. Esters of isononanol are widely used for the production of plasticized polyvinyl chloride for the automobile industry. The isononanols necessary for the purpose are prepared on a large scale by oxonation of isomeric octens, particularly of codibutylene. Phthalic and adipic esters produced from the mixture of isomeric nonanols and polyvinyl chloride plasticized therewith do not satisfy industrial requirements because the volatility of the said esters is too high and the plasticized polyvinyl chloride has too low resistance to cold. These two properties are important particularly in the automobile industry because it is well known that motor-cars are exposed to very marked fluctuations in temperature.
- 40 There was therefore the problem of finding bis-isononyl esters of phthalic acid or of adipic acid which have the lowest possible volatility and are of a type such that polyvinyl chloride plasticized with the said esters has the highest possible resistance to cold.

We have now found that it is advantageous to use, in the form of bis-isononyl esters of phthalic acid or of adipic acid as plasticizers for polyvinyl chloride, isononanols which have been prepared from 2-ethylhexene-1 according to the oxo synthesis by reaction with carbon monoxide and hydrogen at elevated temperature and at superatmospheric pressure in the presence of a carbonyl complex of a metal of group 8 of the Periodic System with or without subsequent hydrogenation.

Bis-isononyl esters of phthalic acid and of adipic acid produced from the isononanols prepared in this way are distinguished by particularly low volatility and moreover by low viscosity which is very advantageous in processing. Moreover polyvinyl chloride materials plasticized therewith have particularly good resistance to cold.

2-ethylhexene-1 is used as starting material and can be readily prepared by dimerization of butene-1 with a trialkylaluminium, 2-ethylhexene-1 is converted into isononanol according to the oxo synthesis by reaction with carbon monoxide and hydrogen at elevated temperature and at superatmospheric pressure in the presence of a carbonyl complex of a metal of group 8 of the Periodic System, with or without subsequent hydrogenation. Carbon monoxide and hydrogen are advantageously used in a ratio by volume of 2:1 to 1:2. A ratio by volume of from 0.8:1 to 1:0.8 has proved to be particularly suitable in industry. The said gas mixture is generally used in an excess of up to 300% with reference to 2-ethylhexene-1. The oxo reaction is advantageously carried out at temperatures of from 140° to 210°C, particularly from 150° to 200°C. It is advantageous to use pressures of from 20 to 350 atmospheres. Particularly good results are obtained at pressures of from 40 to

300 atmospheres. The carbonyl compounds of metals of group 8 of the Periodic System which are used industrially are generally those of cobalt and rhodium. Carbonyl complexes of cobalt have achieved special importance. The metal carbonyl complex used may be modified by additives, for example by secondary or tertiary phosphines such as tri-n-butyl phosphine, tri-n-butyl phosphite or triphenyl phosphine. It is advantageous to use the said metal carbonyl compounds in amounts of from 0.5 to 2% by weight (calculated as metal), based on the amount of 2-ethylhexene-1 used. When a phosphine or phosphite is used as modifying agent, the atomic ratio of metal to phosphorus is advantageously from 1:1 to 1:4.

The resultant oxo reaction mixture (consisting substantially of isononanol and nonanol) may be hydrogenated in order to convert any aldehydes contained therein into the corresponding alcohols. The hydrogenation is carried out advantageously in the presence of a conventional hydrogenation catalyst, particularly in the presence of hydrogenation catalysts containing nickel and/or cobalt. Pressures of from 35 to 300 atmospheres and temperatures of from 120° to 220° are generally used in the hydrogenation.

The isononanol, advantageously purified by distillation, are then esterified with phthalic anhydride or adipic acid, preferably in a molar ratio of from 2:1 to 3:1 at a temperature of from 80° to 240°C in the presence or absence of an esterification catalyst such as sulfuric acid, benzenesulfonic acid, toluenesulfonic acid, organic tin catalysts, antimony trioxide or zinc oxide, and then distilled preferably using an entrainer such as benzene, toluene or another inert hydrocarbon, advantageously at sub-atmospheric pressure.

The bis-isononanol esters of phthalic acid and of adipic acid are useful as plasticizers for polyvinyl chloride. The plasticized polyvinyl chloride material generally contains from 25 to 40% by weight of the said bis-isononyl esters of phthalic or adipic acid. The said esters may be incorporated by a conventional method, for example at temperatures of from 170° to 200°C, in suitable equipment, for example calenders.

The advantageous properties will be illustrated in the following Examples.

EXAMPLE 1.

(a) 1500 g of 2-ethylhexene-1 and 12 g of cobalt hexanoate are placed in a 5-liter autoclave and the air is displaced by sweeping with a gas mixture of equal parts of carbon mon-

oxide and hydrogen. The said gas mixture is then forced in up to 120 atmospheres gauge and heated to 170°C. During the reaction, a pressure of 250 atmospheres gauge is maintained by continuously forcing in more of the said gas mixture. As soon as the pressure remains constant, the reaction mixture is cooled and expanded and 100 g of Raney nickel is added. The mixture is then hydrogenated at 190°C and under a hydrogen pressure of 300 atmospheres gauge until the pressure remains constant. After cooling and expansion, the reaction mixture is fractionated at 1 mm Hg. 1160 g of isononanol is obtained having a refractive index of n_D^{25} 1.4355, a hydroxyl number of 385.9 mg of KOH per gram of isononanol and a carboxyl number of 0.5 mg of KOH per gram of isononanol.

(b) 444 g of phthalic anhydride and 1095 g of the isononanol obtained as above are heated at 200°C for four hours until the acid number is about 5 mg of KOH per gram of substance. The water of reaction formed is continuously removed azeotropically. Then the excess of alcohol is distilled off *in vacuo* at 15 mm Hg up to a bottoms temperature of 150°C. The crude bisisononyl phthalate then has 5% by weight aqueous caustic soda solution added to it at 60°C until a pH of 12 is reached and it is stirred for twenty minutes. The aqueous phase is then separated and the organic phase is washed with water until the acid number is below 0.1 mg of KOH per gram of substance. The ester obtained is distilled with steam at 30 mm Hg and 110°C until it is free from isononanol. Then the ester has 2 g of active carbon added to it and is heated for one hour *in vacuo* at 10 to 20 mm Hg at 120°C. After the active carbon has been separated, 1170 g of bisisononanol phthalate is obtained having the following properties: acid number 0.04 mg KOH/g of substance; saponification number 265 mg KOH/g of substance; refractive index n_D^{25} 1.4855; density 0.973 g/cm³.

(c) The procedure described in 1(b) is followed but 438 g of adipic acid is used instead of phthalic anhydride. After analogous processing, 1110 g of bisisononyl adipate is obtained having the following properties: acid number 0.06 mg KOH/g of substance; saponification number 284 mg KOH/g of substance; refractive index n_D^{25} 1.4496; density 0.9205 g/cm³.

The advantageous properties of the bisisononyl phthalate and adipate thus prepared over isononyl esters of phthalic and adipic acid produced from codibutylene are illustrated in the following Table 1.

TABLE I

Vis = viscosity in centipoises at 20°C according to DIN 51,550;

Vol = volatility in % by weight in two hours at 150°C.

TABLE 1

Ester	Vis	Vol
bisisononyl phthalate from 2-ethylhexene-1	74	0.05
bisisononyl phthalate from codibutylene	169	0.11
bisisononyl adipate from 2-ethylhexene-1	18.9	0.06
bisisononyl adipate from codibutylene	28.7	0.36

EXAMPLE 2.

Polyvinyl chloride is plasticized with the esters indicated in Table 1 on a calender. The exact relative proportions of polyvinyl chloride and ester and the properties of the plasticized polyvinyl chloride may be seen from the following Table 2. The following abbreviations are used in the Table,

BINP=bisisononyl phthalate

BINA=bisisononyl adipate

Codib=from codibutylene

2-eh-1=from 2-ethylhexene-1

(a)=prior to aging

(b)=after aging for eleven days at 90°C in a circulating-air drying cabinet with partial fresh air supply.

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TABLE 2

		BINP		BINA	
		Codib	2-eh-1	Codib	2-eh-1
relative proportions polyvinyl chloride:ester in % by weight		75:25	75:25	75:25	75:25
rolling temperature °C.		170	170	170	170
time in minutes		5	5	5	5
tensile strength (kg/cm ²) (DIN 53,455)	(a)	306	327	262	264
	(b)	314	344	288	280
elongation at break (DIN 53,455)	(%)				
	(a)	222	256	235	254
	(b)	218	249	202	246
cold brittleness temperature in °C (DIN 53,372, tentative standard)	(a)	+5	-15	-28	-35
	(b)	+10	-10	-1	-20
volatility (% by wt) after eleven days at 90°C		-2.5	-0.97	-7.9	-3.62

WHAT WE CLAIM IS:—

1. Polyvinyl chloride containing as plasticizer an isononanol in the form of a bisisononyl ester of phthalic acid or of adipic acid wherein the isononanol has been prepared from 2-ethylhexene-1 according to the oxo synthesis by reaction with carbon monoxide and hydrogen at elevated temperature and at superatmospheric pressure in the presence of a carbonyl complex of a metal of group 8 of the Periodic System. 50
2. Polyvinyl chloride containing as plasticizer an isononanol in the form of a bisisononyl ester of phthalic acid or of adipic acid, wherein the isononanol has been prepared by the method specified in claim 1 and then hydrogenated. 55
3. An isononanol which has been prepared from 2-ethylhexene-1 according to the oxo synthesis by reaction with carbon monoxide and hydrogen at elevated temperature and at superatmospheric pressure in the presence of a carbonyl complex of cobalt or rhodium, with or without subsequent hydrogenation. 60
4. An isononanol as claimed in claim 3 prepared substantially as described in Example 1(a). 65
5. A method of preparing an isononanol wherein 2-ethylhexene-1 is reacted according to the oxo synthesis with carbon monoxide and hydrogen at elevated temperature and at superatmospheric pressure in the presence of a carbonyl complex of a metal of group 8 of the Periodic System. 70
6. A method as claimed in claim 5 wherein the group 8 metal is cobalt or rhodium. 75
7. A method as claimed in claim 5 or 6 wherein the ratio of carbon monoxide to hydrogen is from 2:1 to 1:2 by volume. 80
8. A method as claimed in claim 7 wherein the said ratio by volume is from 1:0.8 to 0.8:1. 85
9. A method as claimed in any of claims 5 to 8 wherein the oxo reaction is carried out at a temperature of from 150° to 200°C.
10. A method as claimed in any of claims 5 to 9 wherein the oxo reaction is carried out at a pressure of from 20 to 350 atmospheres.
11. A method as claimed in claim 10 wherein the oxo reaction is carried out at a pressure of from 40 to 300 atmospheres.
12. A method as claimed in any of claims 5 to 11 wherein the carbonyl complex is modified by an additive.
13. A method as claimed in claim 12 wherein the additive is a secondary or tertiary phosphine.
14. A method as claimed in claim 13 wherein the additive is tri-n-butyl phosphine, tri-n-butyl phosphite or triphenyl phosphine.
15. A method as claimed in any of claims 5 to 14 wherein the metal carbonyl compound is used in an amount (calculated as metal) of from 0.5 to 2% by weight based on the 2-ethylhexene-1.
16. A method as claimed in any of claims 5 to 15 wherein the oxo reaction mixture obtained is hydrogenated.
17. A method as claimed in claim 16 wherein the hydrogenation is carried out in the presence of a conventional hydrogenation catalyst.
18. A method as claimed in claim 16 or 17 wherein the hydrogenation is carried out at a pressure of from 35 to 300 atmospheres and a temperature of from 120° to 220°C.
19. An isononanol when obtained by the method claimed in any of claims 5 to 18.
20. A method of producing a bisisononyl ester wherein an isononanol obtained by the method claimed in any of claims 5 to 18 is esterified with phthalic acid or with adipic acid.
21. A method as claimed in claim 20 carried out substantially as described or illustrated in Example 1(b) or Example 1(c).
22. A bisisononyl ester when obtained by a method as claimed in claim 20 or 21.
23. Polyvinyl chloride which has been plasticized by the use of a bisisononyl ester obtained by a method as claimed in claim 20 or 21 as a plasticizer.

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